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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2019.02

May 01, 2019

Subject: New instrument validation of Shimadzu TOC-L carbon analyzer using acidification with NDIR method for analysis of dissolved inorganic carbon (DIC) in water samples

Effective: July 01, 2018

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1 PURPOSE

This memorandum provides instrument validation data for the determination of dissolved inorganic carbon (DIC) in filtered water samples using acidification and sparging with non-dispersive infrared spectroscopy (NDIR) detection on Shimadzu TOC-L instrumentation. The validation data support the approval of the new instrument and new lab codes and method codes for DIC. Results from a paired sample study are provided to allow data users the ability to compare results from the new instrument with historical results. The new instrumentation for DIC analyses and analyte information were implemented July 1, 2018.

2 BACKGROUND AND SUMMARY

In August 2017, the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) purchased a new Shimadzu TOC-L_{CPH} high sensitivity total organic carbon analyzer for analysis of DIC. The Shimadzu instrument (herein referred to as “TOC-L”) replaces the Tekmar Phoenix 8000 (herein referred to as “Phoenix”) total organic carbon analyzer previously in use at the NWQL. Both new and old instrument platforms utilize acidification to convert DIC to carbon dioxide, which is then sparged from the sample and measured using NDIR. The implementation of the TOC-L represents an instrument validation for DIC. The method is described within SM5310B (Clesceri and others, 1998). DIC was previously analyzed using the same method on the Phoenix instrument, on a custom basis. Following this instrument validation of an approved method, the NWQL will offer DIC analysis using the TOC-L to all customers.

Table 1 describes the new and old instrument platforms. NWQL laboratory codes (LC) and NWIS method codes will change for DIC, but NWIS parameter codes and source methods will remain the same (table 2). The detection limits (DLs), reporting limits (RLs) and analytical ranges have been determined for DIC using the TOC-L, and are also reported in table 2.

Table 1. New and old instrument information for the analysis of DIC at the NWQL.

[NWQL, National Water Quality Lab; DIC, dissolved inorganic carbon; LC, laboratory code; NDIR, non-dispersive infrared spectroscopy]

Instrument name	Instrument manufacturer	Instrument model	Constituents analyzed	Dates in use at NWQL	Method used	Method description
TOC-L	Shimadzu	TOC-L _{CPH}	DIC LC 2625	Starting 07/01/18	SM5310B	Acidification with NDIR
Phoenix	Tekmar	Phoenix 8000	DIC LC 8097	1/10/08 to 6/30/18	SM5310B on custom basis	Acidification with NDIR

Table 2. Parameter codes, method codes, and detection and reporting limits for dissolved organic carbon (DIC) analyzed on the new TOC-L instrument and previously used Phoenix instrument.

[NWIS, National Water Information System; DL, detection limit; RL, reporting limit; RL type code, report level type code; mg/L, milligrams per liter; DLBLK, detection limit report level type code in NWIS set with blank data]

Instrument name	Source method	Lab code	NWIS parameter code	NWIS method code	DL ² (mg/L)	RL ³ (mg/L)	NWIS RL type code
TOC-L	SM 5310B ¹	2625	00691	IR006	0.5	1.0	DLBLK
Phoenix	SM 5310B ¹	8097	00691	OX020	0.2	0.4	DLBLK

¹Clesceri and others, 1998; ²the DL concentration is reported as the “less than” (<) value to NWIS when an analyte is not detected or is detected at a concentration below the DL, as described in USGS Office of Water Quality Technical Memorandum [2010.07](#); ³the RL concentration reported is two times the DL concentration as described by Childress and others, 1999.

Because the TOC-L uses the same method to quantify DIC as was used by the Phoenix, only minimal differences were expected between comparison samples. A two-tailed t-test on paired analyses of 45 environmental samples with detectable concentrations showed no significant differences between the two instruments (section 4.4). These data imply that results for sample analyzed for DIC on the TOC-L, beginning July 1, 2018, are expected to be statistically similar to those that could have been obtained on the Phoenix. All data reported in this validation have met quality control (QC) requirements outlined in the NWQL Quality Management System Report (Stevenson, 2013).

New sample containers are associated with this instrument validation, and data supporting this change are included in this document. Beginning 1 July 2018, the containers used to collect DIC samples should be 3 x 40mL amber glass vials ([N1560](#)).

Transition to the TOC-L instrument will not affect field processing, preservation, or holding times, which remains as follows:

Field filtration: 0.45 micrometer (µm) capsule filter ([Q398FLD](#))
Preservation: chill (< 6°C, but do not freeze)
Holding time: 28 days

2.1 Anticipated analytical requirements

During a typical water year (October 1 to September 30), approximately 1500 surface-water samples are analyzed for DIC using LC 8097. In water years 2008 through 2018, no groundwater samples were submitted for this analysis. DIC concentrations in WY2016 and 2017 ranged from <0.5 to 87.5 mg/L DIC, and approximately 90% of values were between 5 and 60 mg/L DIC.

2.2 Instrument overview

The TOC-L and Phoenix use the same method to analyze directly for DIC. Both convert DIC to aqueous carbon dioxide (CO₂) through acidification, volatilize it through sparging, and subsequently utilize a non-dispersive infrared (NDIR) sensor to detect and quantify the gas. Vendor-supplied NIST-traceable stock solutions of a mixture of sodium carbonate and sodium bicarbonate were used for calibration standards for both instruments. Concentrations of calibration standards used for the TOC-L system during this study were 0.0, 1.0, 2.5, 5.0, 10.0, 25.0 and 50.0 mg/L DIC.

An autosampler is used for all platforms for DIC analysis. The TOC-L autosampler can perform dilutions automatically, and this feature is used to dilute calibration standards, quality-control (QC) standards, and environmental samples as needed. The TOC-L autosampler removes an aliquot of sample from the sample vial and transfers 200 microliters to a sparging vessel containing an acid solution, having a pH between 2 and 3. The sparging vessel on the TOC-L automatically regenerates the acid solution when the pH inside the vessel measures greater than 3, ensuring that all DIC is converted to aqueous CO₂. The aqueous CO₂ is subsequently volatilized by sparging and the total amount is detected by the NDIR. Samples analyzed on the Phoenix system were diluted manually by the analyst, and a consistent volume of acid was added to ensure complete removal of DIC for concentrations within the calibration range (0.2 to 30.0 mg/L DIC).

For the TOC-L, the acidification and sparging process is repeated at least three times, but up to a maximum of four times, for each sample until the TOC-L software calculates that three replicate IR absorbance measurements meet the precision requirements of a standard deviation (SD) of <0.1 mg/L DIC or a coefficient of variation (CV) of <5%. The TOC-L software calculates the average of the three measurements that meet the precision criteria and this value is reported as the TOC-L result for each sample. For the Phoenix, two replicate IR absorbance measurements were performed for each sample and the average was reported.

3 VALIDATION STUDY METHODS

Data collection for the DIC validation study was conducted over an 11-week period in March to May of 2018 and was performed on the TOC-L system. Bias and variability were determined using replicate measurements of QC samples, blanks, blank spikes, surface-water samples, surface-water spikes and surface-water dilutions. QC samples were analyzed interspersed with environmental samples over the course of fifteen analytical batches.

3.1 Comparison of bottle types

Field personnel collected environmental DIC samples in 125 mL amber glass bottles as described for carbon samples in the USGS Field Manual for the Collection of Water Quality Data. DIC samples were field filtered through 0.45 μm capsule filters and chilled upon collection. At the request of the NWQL, customers also collected three 40 mL amber glass vials of several samples to compare to 125 mL amber glass bottles that were previously used to store DIC samples. The new bottle type of three 40 mL amber glass vials allows for up to two replicate re-analyses from unopened 40 mL amber glass vials if needed, improving the precision between results when a sample may need to be re-analyzed for a dilution or QC failure.

3.2 Detection limit evaluation

The new NWQL DL for DIC (0.5 mg/L DIC) was determined on the TOC-L by evaluating a combination of several procedures. MDLs as described by 40 CFR Appendix B Part 136, Revision 2 (U.S. EPA, 2016) were calculated from repeated measurements of a solution with a DIC concentration of 1.0 mg/L DIC and from blanks. Additionally, blank results from throughout the validation were pooled and analyzed to determine blank-limited DLs using the procedures outlined in NWQL Technical Memorandum 15.02 (Williams and others, 2015). In 2015, the NWQL implemented the use of an ASTM software program called DQCALC to determine and verify detection limits. The DQCALC software algorithm (ASTM, 2010) was utilized to determine a DIC DL based on calibration standards run on the instrument in March through May of 2018.

3.3 Evaluating bias and variability in standards and QC samples

Third-party check (TPC) solutions were made from sodium carbonate anhydrous and sodium bicarbonate anhydrous salts at the NWQL, at concentrations of 5.0 and 25.0 mg/L DIC and these solutions were analyzed at least once per run to assess bias and variability. Continuing calibration verification (CCV) standards were also analyzed at a frequency of at least once per every ten samples throughout the validation study. The CCV solutions were diluted from the NIST-certified pre-made DIC solutions used for calibration, as described in section 2.2.

3.4 Evaluating bias and variability in surface-water and surface-water matrix spikes

A large volume of a single surface-water sample was collected from the output of Ralston Reservoir located in Golden, CO to determine the day to day variability of the DIC method and to calculate bias with respect to matrix spike recovery. This single surface-water is herein referred to as the local test-sample. The local test-sample was filtered through a 0.45 μm capsule filter and stored at $<6^{\circ}\text{C}$ for no longer than 28 days. The local test-sample was repeatedly analyzed for DIC diluted, unspiked, and spiked with 25.0 mg/L DIC using a 1,000 mg/L DIC sodium carbonate and sodium bicarbonate stock solution. Six to nine measurements of the unspiked local test-sample, diluted unspiked local test-sample, and spiked local test-sample were taken on the TOC-L over the course of the validation study.

Several environmental surface-water samples submitted by customers were also chosen for duplicate and spike/spike duplicate sample measurements on the TOC-L. Seven sets of matrix

duplicates and spike/spike duplicate pairs were analyzed. Selected samples were spiked with the same 1,000 mg/L DIC solution as was used for spiking the surface-water sample described in the previous paragraph. For spikes of 5.0 mg/L DIC, 19.9 mL of sample was mixed with 0.1 mL spiking solution, which resulted in the sample being diluted by 0.5 percent. For spikes of 25.0 mg/L DIC, 19.5 mL of sample was mixed with 0.5 mL spiking solution, which resulted in the sample being diluted by 2.5 percent. Samples were spiked at less than 5 percent sample volume and no spiking correction factor was incorporated into the calculation of the spike percent recoveries.

3.5 Comparison of paired analyses of samples analyzed on TOC-L and Phoenix

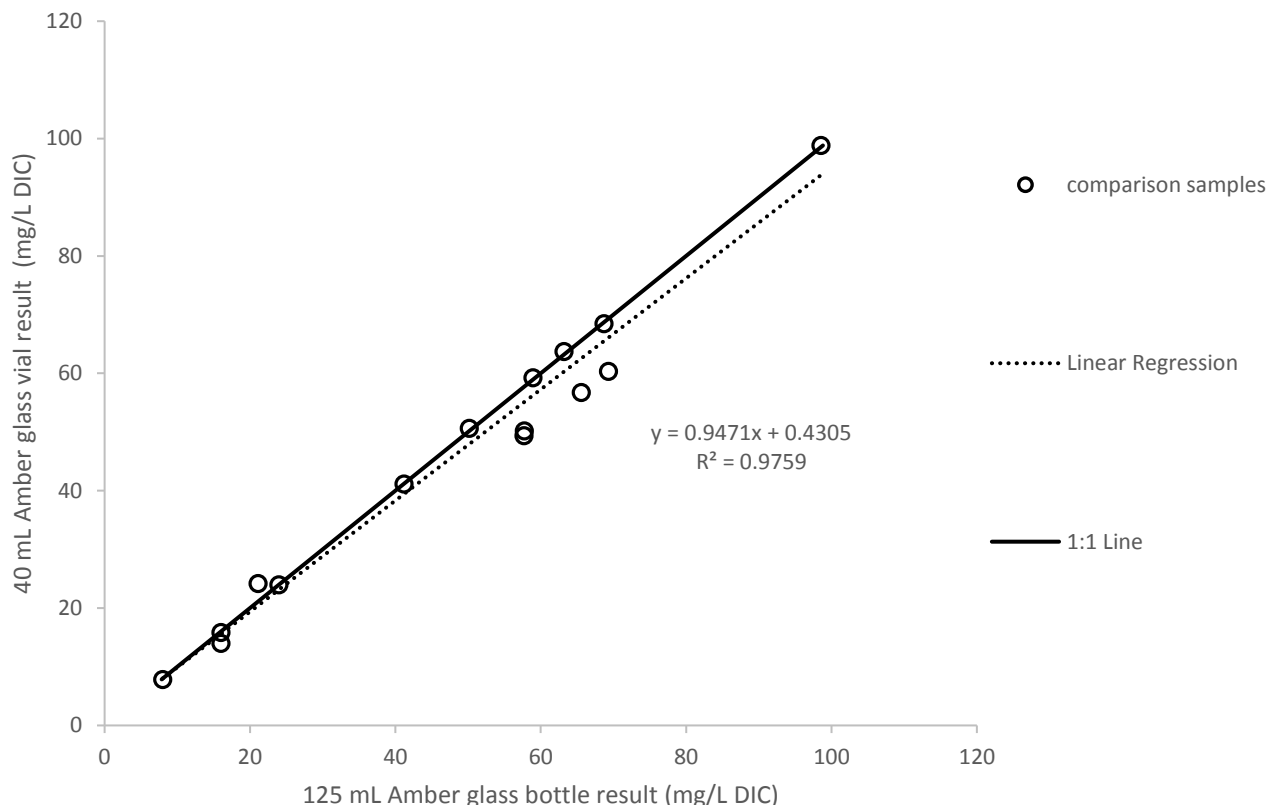
The DIC concentrations of 81 environmental surface-water samples from many unique geographical areas across the United States were determined on the new and old platforms (see attachment 1 for a list of samples and analytical results). Environmental comparison samples were selected from those logged in at the NWQL for DIC analysis and are representative of the matrices and concentrations projected to be analyzed on an annual basis. Samples were analyzed on the TOC-L and Phoenix on the same day.

4 RESULTS AND DISCUSSION

4.1 Comparison of bottle types

Customers submitted fifteen replicate samples collected in the new 40mL amber glass vial and the previously used 125 mL amber glass vial. The NWQL analyzed the samples from both containers on the TOC-L. The results of this bottle comparison (figure 1) demonstrate comparability between sample storage containers. Starting on October 1, 2018 only the three 40 mL amber glass vials will be accepted for the DIC analysis. DIC samples submitted in the old 125 mL bottle after this date will be qualified as improperly collected.

Figure 1. Dissolved inorganic carbon (DIC) measurements from environmental samples in the previously used 125 mL glass amber bottles and the 40 mL glass amber vials in milligrams per liter dissolved inorganic carbon (mg/L DIC) (n=15). Data are plotted next to a 1:1 reference line.



4.2 Detection limit study for DIC

The NWQL detection limit of 0.5 mg/L DIC on the TOC-L was evaluated using several different methods as described in section 3 and table 3. An EPA-style spike-based detection limit calculation (U.S. EPA, 2016) using replicate analyses of a solution of 1.0 mg/L DIC, resulted in a calculated DL of 0.3 mg/L DIC. A DQCALC algorithm multi-concentration DL (ASTM, 2010) was determined using 13 replicate reagent water spikes at each concentration level, which resulted in a calculated DL of 0.1 mg/L DIC. The highest DL determination resulted from a average + $s \times t$ blank-based determination (U.S. EPA, 2016), 0.5 mg/L DIC. The NWQL has assigned a DL of 0.5 mg/L DIC on the TOC-L with an NWIS RL type code of DLBLK to indicate that the DL was determined using a blank-based approach. This DL represents a change from the previous DL of 0.2 mg/L DIC on the Phoenix.

The NWQL assesses DLs on an annual basis. After one year of collecting analytical, the DLs for DIC will be reexamined and may be changed depending on method performance.

Table 3. Evaluation of approaches for determining the detection limit for dissolved inorganic carbon (DIC) using the Shimadzu TOC-L instrument

DL determination method	n	Average result (mg/L)	Standard deviation (mg/L)	Calculated DL (mg/L)
Spike-based $s \times t$ determination using 1.0 mg/L solution ¹	38 (t = 2.43)	1.1	0.1	0.3
Blank-limited determination, Average + $s \times t$ ¹	97 (t = 2.37)	0.1	0.2	0.5
Blank-limited determination, 2nd highest blank value ²	97	--	--	0.4
DQCALC determination ³	13 at each concentration	--	--	0.1
NWQL assigned	n/a	--	--	0.5

¹ U.S. Environmental Protection Agency, 2016

² Williams and others, 2015

³ American Society for Testing and Materials, 2010

4.2 Bias and variability of repeated DIC measurements in standards

Bias and variability in DIC analyses using the TOC-L were assessed for third-party check (TPC) and continuing calibration verification (CCV) standards (table 4). Bias is assessed by comparing the observed results to the expected results, expressed either as concentration or percent recovery. Variability is characterized by the standard deviation and relative standard deviation and is expected to decrease as concentration increases across the analytical range. TPC standards demonstrated a slight low bias, with the observed mean concentration for each standard falling within ± 4 percent of the expected concentrations. The CCV standards demonstrated minimal bias and variability. Bias and variability of the CCV standard purchased as pre-made stock solutions show slightly better observed bias and variability than the TPC standards made in-house at the same concentrations.

Table 4. Bias and variability of DIC in standards prepared with reagent water

[DIC, dissolved inorganic carbon; TPC, third party check solution prepared from sodium carbonate anhydrous and sodium bicarbonate anhydrous salts; CCV, continuing calibration verification standard made from diluted NIST-certified stock solution; %, percent; RSD, relative standard deviation; DL, detection limit; n, number of analyses; mg/L, milligrams per liter; n/a, not applicable]

Standard name	Expected concentration (mg/L)	n	Results observed in DIC standards			
			Mean concentration (mg/L)	Standard deviation (mg/L)	RSD (%)	Mean recovery (%)
TPC 5	5.0	51	4.8	0.4	8.1	96.6
TPC 25	25.0	45	24.5	0.7	3.0	98.1
CCV 2.5	2.5	55	2.6	0.2	5.9	104.0
CCV 5	5.0	37	5.0	0.2	4.8	100.8
CCV 10	10.0	29	9.8	0.5	5.4	98.1
CCV 25	25.0	18	24.7	0.4	1.4	98.8

4.3 Bias and variability of repeated DIC measurements in surface-water samples and matrix spikes

Variability of DIC analyses using the new instrumentation was assessed using repeated measurements of the local test-sample and matrix spikes of the local test-sample prepared as described in section 3.4. Results are reported in table 5. RSDs were less than 10%, with the highest RSD being for concentrations near the detection limit of 0.5 mg/L DIC. The local test-sample spiked with 25.0 mg/L DIC demonstrated lower recoveries than were observed in similar spikes in reagent water (TPC 25, section 4.2, tables 4 and 5). Low DIC recoveries are possible when spiking an environmental water sample with carbonate and bicarbonate spiking solution because calcite, and possibly other insoluble carbonate minerals, may form. Water samples that contain elevated concentrations of calcium ions (Ca^{2+}) are subject to the formation of calcite (CaCO_3) upon the addition of the 1000 mg/L DIC solution composed of sodium carbonate and sodium bicarbonate salt through the following carbon dioxide-calcium carbonate equilibria equation: $\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3(\text{s}) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$ (Manahan, 2010). If the solution is oversaturated with calcite, it precipitates out of solution and sinks to the bottom of the vial, causing a loss of carbonate and resulting in a low DIC spike recovery. Many carbonates are insoluble, and this addition of the spike solution could cause precipitation of many species of insoluble carbonates. It is important to note that this is a solubility limitation, not an indication of matrix effects during analysis. Therefore, matrix spikes of environmental samples are not recommended for this analysis. Although matrix spikes are not recommended, environmental

sample duplicates are appropriate sample-level QC and will be included in all analytical batches at the NWQL with a frequency of one sample/duplicate pair per batch.

Table 5. Variability and bias of DIC in local test-sample, diluted local test-sample, and spiked local test-sample

[DIC, dissolved inorganic carbon; %, percent; RSD, relative standard deviation; n, number of analyses; mg/L, milligrams per liter; n/a, not applicable]

Sample matrix	Expected concentration (mg/L)	n	Results observed in surface-water samples and matrix spikes			
			Mean concentration (mg/L)	Standard deviation (mg/L)	RSD (%)	Mean recovery (%)
Local test-sample (Surface-water)	--	9	17.2	0.2	1.1	--
Diluted local test-sample (Surface-water diluted 1:10 with reagent water)	1.7 (1/10 of the concentration in corresponding surface-water sample)	6	1.6	0.2	9.0	93.0
Spiked local test-sample (Surface-water spiked with solution made from sodium carbonate and sodium bicarbonate salts)	42.2 (25.0 plus the concentration in corresponding surface-water sample)	8	39.9	2.4	6.0	86.6

During the DIC validation study, nine additional environmental samples from various sites were analyzed for un-spiked duplicate analyses and matrix spike/spike duplicate analyses. Samples varied in matrix and native DIC concentration. Spikes and spike duplicates were spiked with 25.0 mg/L DIC using the 1,000 mg/L DIC TPC solution made in-house by the NWQL. The median spike recovery for the samples was 92 percent. Duplicate samples for DIC had a median relative percent difference (RPD) of 0.8 percent and spike duplicates had a median RPD of 0.2 percent. These data indicate the precision expected in duplicate samples analyzed on the same day. As was discussed in the previous paragraph, routine spiking of environmental samples is not advised because of the potential for precipitation of a carbonate solid.

4.4 Comparison data from paired environmental samples

81 environmental samples were analyzed on the TOC-L and Phoenix instruments (attachment 1). The mean percent difference between platforms for samples with concentrations above 0.5 mg/L DIC was -1.0 percent. Samples with results below the TOC-L DL (n=4) were not included in figures from this section, but the data for all samples are presented in Attachment 1.

Through the implementation of the TOC-L, the DIC upper analytical range increased from 30.0 mg/L (Phoenix) to 50.0 mg/L (TOC-L). The change in analytical range resulted in many

environmental comparison samples to be run diluted on the Phoenix, but undiluted on the TOC-L. All data above the detection limit on the TOC-L are presented in Figure 2. A two-tailed paired t-test established that at the 95% confidence level, there was no significant difference between results from the two instrument platforms.

In figure 3, the percent differences in concentration between the two platforms are plotted against concentration, and the random scatter of the plot demonstrates that there is no consistent bias to the differences. The average percent difference for samples between the TOC-L and the Phoenix was -1.0 ± 2.2 percent, using a 99 percent confidence interval.

Figure 2. Dissolved inorganic carbon (DIC) measurements from environmental samples on the TOC-L and Phoenix instruments in milligrams per liter dissolved inorganic carbon (mg/L DIC) (n=77). Data are plotted next to a 1:1 reference line.

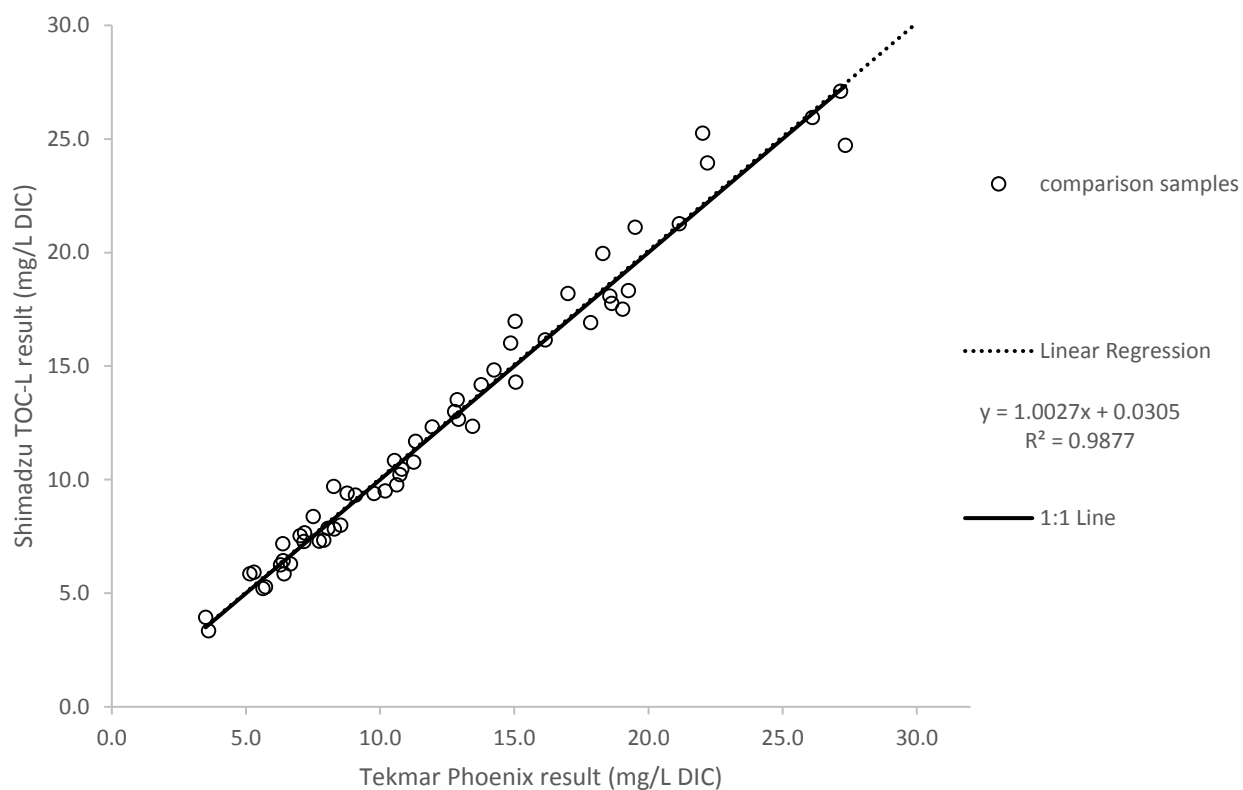
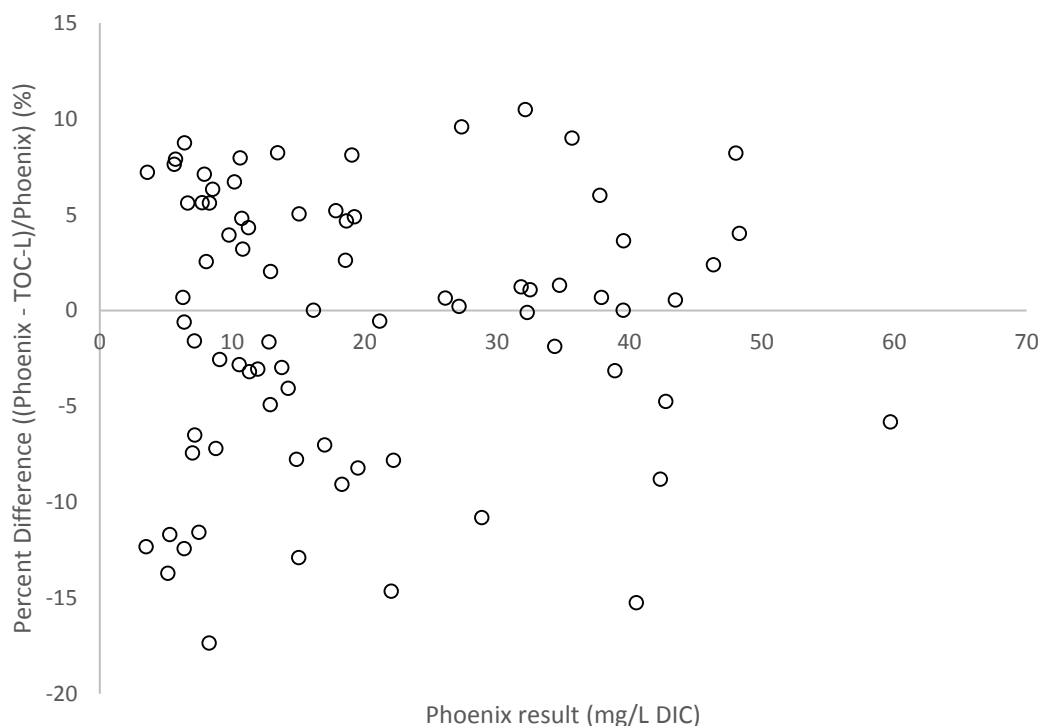


Figure 3. Percent difference of dissolved inorganic carbon (DIC) measurements from environmental samples on the TOC-L and Phoenix instruments versus the DIC measured on the Phoenix, in milligrams per liter dissolved inorganic carbon (mg/L DIC) (n=77).



5 SUMMARY

Comparison data suggest that customers will experience little to no change in analytical results for DIC analyses. Both instrument platforms produce data that are of acceptable quality for inorganic carbon analyses of this nature, as demonstrated by the acceptable performance of the QC samples. Results from customer samples analyzed on the TOC-L beginning July 1, 2018 are expected to be statistically similar, at a 95% confidence interval, to those that could have been obtained on the Phoenix.

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7 ATTACHMENT

Attachment 1- Measured dissolved inorganic carbon (DIC) on both the Tekmar Phoenix (existing instrument) and Shimadzu TOC-L (replacement instrument)

/signed/
Jeff McCoy, Chief
National Water Quality
Laboratory

Supersedes: N/A

Key words: dissolved inorganic carbon, DIC, bias, variability, instrument validation

Distribution: by Rapi-Note announcement

Posted to <http://wwwnwql.cr.usgs.gov/USGS> (the NWQL USGS-visible intranet; internal USGS access only) and <http://nwql.usgs.gov/Public> (the NWQL public internet)

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Attachment 1

Measured dissolved inorganic carbon (DIC) on both the new Shimadzu TOC-L and Tekmar Phoenix instruments

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Phoenix minus measurement on TOC-L) divided by measurement on Phoenix times 100 percent; WS, surface-water sample; OAQ, artificial quality-control sample (blank water); N/A, not applicable]

LC	Medium	LabID	Phoenix result (mg/L)	TOC-L result (mg/L)	Percent difference
8097	OAQ	20180540166	0.3	<0.5	N/A
8097	OAQ	20180650005	0.3	<0.5	N/A
8097	OAQ	20180670058	0.3	<0.5	N/A
8097	OAQ	20180470082	0.5	<0.5	N/A
8097	WS	20180540026	3.5	3.9	-12
8097	WS	20180680049	3.6	3.3	7
8097	WS	20180660062	5.1	5.9	-14
8097	WS	20180470010	5.3	5.9	-12
8097	WS	20180680048	5.6	5.2	8
8097	WS	20180670030	5.7	5.3	8
8097	WS	20180810038	6.3	6.2	1
8097	WS	20180540027	6.4	7.2	-12
8097	WS	20180810037	6.4	6.4	-1
8097	WS	20180580025	6.4	5.9	9
8097	WS	20180680121	6.7	6.3	6
8097	WS	20180470031	7.0	7.5	-7
8097	WS	20180810039	7.2	7.3	-2
8097	WS	20180820026	7.2	7.7	-6
8097	WS	20180470080	7.5	8.4	-12
8097	WS	20180680095	7.7	7.3	6
8097	WS	20180580016	7.9	7.3	7
8097	WS	20180670031	8.0	7.8	3
8097	WS	20180540039	8.3	9.7	-17
8097	WS	20180680096	8.3	7.8	6
8097	WS	20180540216	8.5	8.0	6
8097	WS	20180860017	8.8	9.4	-7
8097	WS	20180860018	9.1	9.3	-3
8097	WS	20180680037	9.8	9.4	4
8097	WS	20180580017	10.2	9.5	7
8097	WS	20180860019	10.5	10.8	-3
8097	WS	20180660082	10.6	9.8	8
8097	WS	20180540168	10.7	10.2	5
8097	WS	20180680166	10.8	10.5	3
8097	WS	20180540145	11.2	10.8	4
8097	WS	20180820071	11.3	11.7	-3
8097	WS	20180860079	11.9	12.3	-3
8097	WS	20180860027	12.8	13.0	-2
8097	WS	20180810005	12.9	13.5	-5
8097	WS	20180680120	12.9	12.7	2
8097	WS	20180540200	13.4	12.3	8

Attachment 1

Measured dissolved inorganic carbon (DIC) on both the new Shimadzu TOC-L and Tekmar Phoenix instruments - Continued

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Phoenix minus measurement on TOC-L) divided by measurement on Phoenix times 100 percent; WS, surface-water sample; OAQ, artificial quality-control sample (blank water); N/A, not applicable]

LC	Medium	LabID	Phoenix result (mg/L)	TOC-L result (mg/L)	Percent difference
8097	WS	20180820030	13.8	14.2	-3
8097	WS	20180820037	14.2	14.8	-4
8097	WS	20180470081	14.9	16.0	-8
8097	WS	20180540016	15.0	17.0	-13
8097	WS	20180540164	15.1	14.3	5
8097	WS	20180670070	16.2	16.2	0
8097	WS	20180540015	17.0	18.2	-7
8097	WS	20180540165	17.8	16.9	5
8097	WS	20180470113	18.3	20.0	-9
8097	WS	20180660088	18.6	18.1	3
8097	WS	20180720042	18.6	17.8	5
8097	WS	20180580018	19.0	17.5	8
8097	WS	20180650013	19.3	18.3	5
8097	WS	20180540095	19.5	21.1	-8
8097	WS	20180820029	21.1	21.3	-1
8097	WS	20180650021	22.0	25.2	-15
8097	WS	20180520032	22.2	23.9	-8
8097	WS	20180660090	26.1	25.9	1
8097	WS	20180670053	27.2	27.1	0
8097	WS	20180580024	27.3	24.7	10
8097	WS	20180540096	28.9	32.0	-11
8097	WS	20180660092	31.8	31.4	1
8097	WS	20180670059	32.2	28.8	10
8097	WS	20180720072	32.3	32.3	0
8097	WS	20180670045	32.5	32.2	1
8097	WS	20180810044	34.4	35.0	-2
8097	WS	20180670054	34.7	34.3	1
8097	WS	20180670061	35.7	32.5	9
8097	WS	20180740042	37.8	35.5	6
8097	WS	20180850001	37.9	37.6	1
8097	WS	20180820076	38.9	40.1	-3
8097	WS	20180670043	39.5	39.5	0
8097	WS	20180660113	39.6	38.1	4
8097	WS	20180820074	40.5	46.7	-15
8097	WS	20180540051	42.4	46.1	-9
8097	WS	20180740049	42.8	44.8	-5
8097	WS	20180820075	43.5	43.3	1
8097	WS	20180850002	46.4	45.3	2
8097	WS	20180540097	48.1	44.1	8
8097	WS	20180720088	48.3	46.4	4
8097	WS	20180530016	59.7	63.2	-6

